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<p>(21) International Application Number: PCT/US95/02095 (22) International Filing Date: 16 February 1995 (16.02.95) (30) Priority Data: 08/258,329 10 June 1994 (10.06.94) US (71) Applicant: THE MEAD CORPORATION [US/US]; Mead World Headquarters, Courthouse Plaza Northeast, Dayton, OH 45463 (US). (72) Inventors: BRAMMER, S., Thomas; The Mead Corporation, Mead World Headquarters, Courthouse Plaza Northeast, Dayton, OH 45463 (US). CAMILLUS, Joseph, C.; The Mead Corporation, Mead World Headquarters, Courthouse Plaza Northeast, Dayton, OH 45463 (US). JOHNSON, Mark, A.; The Mead Corporation, Mead World Headquarters, Courthouse Plaza Northeast, Dayton, OH 45463 (US). LIPPKE, William; The Mead Corporation, Mead World Headquarters, Courthouse Plaza Northeast, Dayton, OH 45463 (US). TAYLOR, John, M.; The Mead Corporation, Mead World Headquarters, Courthouse Plaza Northeast, Dayton, OH 45463 (US). TERRY, Darrell, A.; The Mead Corporation, Mead World Headquarters, Courthouse Plaza Northeast, Dayton, OH 45463 (US).</p>		<p>(74) Agents: LEVY, Mark, P. et al.; Thompson, Hine and Flory, 2000 Courthouse Plaza N.E., P.O. Box 8801, Dayton, OH 45401-8801 (US). (81) Designated States: AU, CA, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p>
<p>(54) Title: SELF-CONTAINED IMAGING ASSEMBLY AND METHOD FOR FORMING IMAGES THEREIN</p> <div data-bbox="324 1134 1380 1533"></div> <p>(57) Abstract</p> <p>A self-contained photohardenable imaging assembly comprising a first transparent support, a second opaque support and an imaging layer comprising a developer material and a plurality of photohardenable microcapsules, said microcapsules containing a color former and a photohardenable composition disposed between the first transparent support and the second opaque support, wherein the second opaque support is bonded to the imaging layer by a layer of adhesive.</p>		

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SELF-CONTAINED IMAGING ASSEMBLY AND METHOD FOR FORMING IMAGES THEREIN

BACKGROUND OF THE INVENTION

The present invention relates to a self-contained imaging assembly and, more particularly, to an improved self-contained imaging assembly in which a composition comprising photohardenable microcapsules and developer material are disposed between a first transparent support and a second support which may be opaque or transparent to form a sealed assembly. The assembly is image-wise exposed to actinic radiation and subjected to a uniform rupturing force to provide an image in said composition which is visible against the second opaque support when viewed through the first transparent support or, if the second support is transparent, the image will be viewed as a transparency.

Photohardenable imaging systems employing microencapsulated radiation sensitive compositions are the subject of commonly assigned U.S. Patent Nos. 4,399,209 and 4,416,966 as well as co-pending U.S. Patent Application Ser. No. 320,643, filed January 18, 1982. These imaging systems are characterized in that an imaging sheet including a layer of microcapsules containing a photohardenable or photosoftenable photohardenable composition in the internal phase is image-wise exposed to actinic radiation. In the most typical embodiments, the photohardenable composition is a photopolymerizable composition including a polyethylenically unsaturated compound and a photoinitiator and is encapsulated with a color former. Exposure to actinic radiation hardens the internal phase of the microcapsules. Following exposure, the imaging sheet is subjected to a uniform rupturing force

by passing the sheet through the nip between a pair of pressure rollers.

Commonly assigned U.S. Patent No. 4,440,846 discloses a self-contained imaging sheet in which the encapsulated color former and the developer material are co-deposited on one surface of a single substrate as one layer or as two contiguous layers. Upon passing the self-contained copy sheet through pressure rollers in contact with the copy sheet, the microcapsules image-wise rupture and release internal phase whereupon the color former migrates to the developer material where it reacts with the developer material and forms a colored image.

U.S. Patent No. 4,766,050, commonly assigned, teaches an imaging system comprising a support, a layer containing microcapsules, a layer of developer material, and a layer containing an opacifying agent. The opacifying agent can form a separate layer or can be part of the layer containing the microcapsules or both.

SUMMARY OF THE INVENTION

The present invention like the imaging system disclosed in U.S. Patent No. 4,766,050 comprises a support, a layer of microcapsules containing a photohardenable composition and a color former as an internal phase, a layer containing developer, and an opacifying agent. Unlike the aforementioned system, the self-contained imaging system of the present invention calls for the opacifying agent when present to be incorporated into a support, namely, the second support which provides a background for the image ultimately formed in the microcapsule layer. Upon image-wise exposure, the microcapsules are ruptured and the color former is image-wise released from the ruptured microcapsules. It is then transported to the developer material with which it reacts to form an image which is visible against the opaque second support when viewed through the transparent first support.

In another embodiment of invention, both the first support and the second support are transparent allowing the image to be viewed as a transparency through a projector such as an overhead projector or a slide projector. In a preferred embodiment of the invention, the developer and the photohardenable microcapsules are in the same layer. Furthermore, in the self-contained imaging system of the present invention, the imaging system is sealed between the two support members which form the upper and lower layers. This prevents the developer material and the chemicals in the microcapsules from contacting persons during handling and, depending on the nature of the supports, may prevent oxygen from permeating into the photohardenable material. This format also provides a glossy "photographic" image.

A principal object of the present invention is to provide an improved and convenient self-contained imaging assembly which provides an image against a white background as viewed through a transparent support or to provide a transparency when both front and back supports are transparent, and which is sealed to prevent contact of irritating chemicals by persons handling the assembly.

One embodiment of the invention is a self-contained imaging system comprising a first support and a second support, wherein the first support is transparent and is coated on one surface with a layer comprising a developer material and photohardenable microcapsules and the second support is either opaque or transparent and is coated on one surface with an adhesive. The first transparent support is bonded to the second support such that the layer containing the developer and the microcapsules is disposed in a facing relation with the adhesive layer to form a laminate. In accordance with this embodiment wherein the first support is transparent and the second support is opaque, the color former, upon rupture of the microcapsules, reacts with the developer material to

form an image which is visible against the opaque support when viewed through the transparent support. In accordance with the embodiment wherein both first and second supports are transparent, the image may be viewed as a transparency.

In another embodiment, a self-contained imaging system is provided comprising a first support and a second support, wherein the first support is a transparent support coated on one surface with a layer of developer material and the second support is either opaque or transparent and is coated on one side with a layer of radiation sensitive microcapsules. The first support is assembled with the second support such that the developer layer is disposed in a facing relation with the microcapsule layer on the second support, and the first support is sealed to the second support along a predetermined border at the periphery of the assembly. The layer containing microcapsules and the layer containing developer material are positioned such that upon rupturing the microcapsules, the color former transfers to the developer layer to form an image. Where the first support is transparent and the second support is opaque, the image is visible against the opaque support when viewed through the first transparent support. Where both supports are transparent, the image is viewed as a transparency preferably using an overhead or slide projector.

In another embodiment of the present invention, there is provided a method for forming an image which comprises exposing the microcapsule layer through the transparent support, subjecting the self-contained imaging system to pressure such that the microcapsules rupture and the color former is image-wise transferred to the developer, and viewing the resulting image against the opaque support or as a transparency.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of an imaging system of the present invention.

FIG. 2 is a cross-sectional view of FIG. 1 after exposure and microcapsule rupture.

FIG. 3 is a cross-sectional view of an imaging system of the present invention.

FIG. 4 is a cross-sectional view of another aspect of the imaging system of FIG. 3.

FIG. 5 is a cross-sectional view of still another aspect of the imaging system of FIG. 3.

FIG. 6 is a cross-sectional view of FIG. 4 after exposure and microcapsule rupture.

FIG. 7 is a perspective view of the imaging sheet of FIG. 3 showing the border of the first transparent support and the second opaque support sealed at the periphery of the assembly with the various layers exposed in a peeled back array.

DETAILED DESCRIPTION OF THE INVENTION

As illustrated in FIG. 1 and in accordance with one embodiment of the present invention, a self-contained imaging system 1 comprises in order: a first transparent support 10, an imaging composition 12 comprising photohardenable microcapsules 14 and a developer material 16, a layer of adhesive 18, and a second support 20 which may or may not contain an opacifying agent 26. By image-wise exposing this unit to actinic radiation, the microcapsules are differentially hardened in the exposed areas as taught in U.S. patent Nos. 4,399,209 and 4,440,846. The exposed unit is subjected to pressure to rupture the microcapsules. FIG. 2 illustrates the self-

contained imaging system of FIG. 1 after exposure and rupture of the microcapsules 14. Ruptured microcapsules 22 release a color forming agent which reacts with the developer material 16 to form an image 24. Typically, the microcapsules will consist of three sets of microcapsules sensitive to red, green and blue light and containing cyan, magenta and yellow formers, respectively, as taught in U.S. patent No. 4,772,541.

In the embodiment of Figs. 1 and 2, layer 12 contains a mixture of a developer material and photohardenable microcapsules. This layer typically contains about 20 to 80% (dry weight) of the developer, about 80 to 20% (dry weight) microcapsules and 0 to 20% binder. The layer is typically applied in a dry coat weight of about 8 to 20% g/cm². An example of such a coating formulation is illustrated in Example 2 below.

In the self-contained photohardenable imaging assembly as shown in FIG. 1, the first support 10 is preferably a transparent polyethylene terephthalate (PET) support coated on one surface with the aforesaid mixture. The second support 20 is preferably an opaque support such as polyethylene terephthalate (PET) containing an opacifying agent (black or white), paper or paper lined with film (polyethylene, polypropylene, polyester, etc.). Most preferably the opaque support is a polyethylene terephthalate support containing about 10% titanium dioxide to form a bright white colored opaque support. This support is commercially available from ICI, Ltd. under the product designation Melinex.

To assemble the second opaque support with the first transparent support, the second opaque support is coated on one surface with an adhesive 18. The first transparent support 10 is assembled with the second opaque support 20 such that the imaging layer 12 is disposed in a facing relation with the adhesive layer 18 to form a

laminate. Upon exposure to actinic radiation followed by an application of uniform rupturing force, an image is formed which is viewed through the transparent support 10 against the bright white colored opaque support 20.

The adhesive useful in this present invention may be an aqueous-based adhesive such as Aerosett 2177 or Aerosett 2550 both of which are commercially available from Ashland Chemical Co., PD 0681, AP 6903, and W 3320 available from H.B. Fuller, or a solvent-based adhesive such as PS 508 sold by Ashland Chemical Co. The adhesives may be used separately or in combination. Preferably, the adhesive is transparent or translucent and most preferably it is a transparent aqueous-based adhesive which remains clear even after subjecting the assembly to radiation and pressure necessary to image-wise expose and rupture the microcapsules. The amount of the adhesive will vary depending on the nature of the adhesive and the support. The adhesive is generally applied in an amount of about 2 to 20 g/cm².

The first transparent support through which the image is viewed can be formed from any transparent polymeric film. A film will be selected which provides good photographic quality when viewing the image. Preferably, a film will be used which is resistant to yellowing. The preferred substrate useful in the self-contained imaging system of the present invention is polyethylene terephthalate (PET) which is a clear polymeric material. Polyethylene terephthalate can be used unaltered as the first and second transparent supports when a transparency is desired. In a preferred embodiment of the invention, the opaque support is white polyethylene terephthalate which contains an opacifying agent as defined above. Typically, each of the PET supports has a thickness of about 2 to 4 mils.

In manufacturing the laminate, it is important not to rupture the microcapsules. This can be accomplished by laminating the layers of adhesive and developer/microcapsules between rubber rolls at a pressure which activates the adhesive but does not rupture the microcapsules.

In a preferred embodiment, the opaque second support is sufficiently opaque so that when a self-contained imaging sheet is exposed to radiation through the transparent support, the opaque support is effective to prevent the radiation from penetrating to other imaging sheets which may be stacked behind the imaging sheet during the exposure step. However, if the units are not exposed in a stacked formation, the opacity of the support is not critical so long as the support provides the desired background. When both supports are transparent, each self-contained imaging assembly must be separated from the other by an opaque member such as an opaque sheet or backing which is easily separated from the imaging sheet.

Generally, the opaque support will be available commercially. Some products which are useful include paper, cardboard, polyethylene, polyethylene-coated paper, etc. These products are composites or admixtures of the polymer and the pigment in a single layer, films or coated papers. Alternatively, the opacifying agent can be provided in a separate layer underlying or overlying a polymer film such as PET. The opacifying agent employed in these materials is an inert, light-reflecting material which exhibits a white opaque background. Materials useful as the opacifying agent include inert, light-scattering white pigments such as titanium dioxide, magnesium carbonate or barium sulfate. In a preferred embodiment the opacifying agent is titanium dioxide.

Another embodiment of the present invention is illustrated in FIG. 3 which shows a self-contained imaging

system 2 which comprises in order, a first support 30, a layer 32 containing a developer material 34, a layer 38 of photohardenable microcapsules 36, and a second support 40 which may or may not contain an opacifying agent 42. The microcapsule layer typically contains about 60 to 90% capsules and is coated in a dry weight of about 4 to 12 g/m². As shown in FIG. 4, a self-contained imaging system 3 in a preferred aspect of this embodiment comprises in order a first support 30, a developer layer 32 containing a developer material 34, a layer 38 of photohardenable microcapsules 36, a subbing layer 44, and a second support 40 which may or may not contain an opacifying agent 42. In another preferred aspect of this embodiment as illustrated in FIG. 5, a self-contained imaging system 4 comprises in order: a first support 30, a developer layer 32 containing a developer material 34, a layer 38 containing photohardenable microcapsules 36 and a spacer material 46, a subbing layer 44, and a second support 40 which may or may not contain an opacifying agent 42.

Images are formed in the present invention in the same manner as described in U.S. Patent No. 4,440,846. FIG. 6 illustrates the image-wise exposure of the imaging system 3 of FIG. 4 through transparent support 30 which produces exposed microcapsules 36 and unexposed microcapsules 48 in the microcapsule layer 38. Upon subjecting the imaging system 3 to a uniform rupturing force such as by passage through a pair of pressure rollers, the unexposed microcapsules 48 rupture and release the internal phase of the microcapsules containing monomer and color former. The color former migrates as shown by the arrows to the developer layer 32 where it reacts with the developer 34 in developer layer 32 to produce a colored image 50. The colored image 50 can be viewed through the first transparent support 30 either against an opaque second support 40 containing opacifying agent 42 which

provides a white background for the colored image 50 or as a transparency when both supports are transparent.

In another aspect of the invention, as illustrated in FIG. 7, the self-contained imaging assembly 2 of the present invention in which the developer and the photohardenable microcapsules are coated in separate layers on different supports, is sealed along a border 52 at the peripheral edges of the assembly. The configuration illustrated in FIG. 7 represents one aspect of the invention which comprises in order, a first support 30, a developer layer 32 containing a developer material 34, a layer 38 containing photohardenable microcapsules 36 and a second support 40 which may or may not contain an opacifying agent 42. FIG. 7 further illustrates a white tape 54 which forms a frame around the self-contained imaging assembly 2.

The bonding of the peripheral edges of the self-contained assembly can be accomplished by any of the conventional means used to seal polymeric materials such as polyethylene terephthalate. For example, films can be sealed using an adhesive or they may be heat sealed together or they can be sealed by any other technique. Preferably, the PET is sealed using a heat sealing method such as a heat knife.

When the microcapsules are provided as a separate layer from the developer, it is advantageous to prevent the microcapsules from picking off during development. A binder such as polyethylene oxide (PEO) having a molecular weight of about 500,000 can be incorporated in the microcapsule layer to prevent "pick off" of the microcapsules from the opaque support during development. A particular useful binder is poly(2-ethyl-2-oxazoline) available under the tradename, aquazol, from Polymer Chemistry Innovations, Inc. Generally, the binder is added to the microcapsule layer in an amount of about 2 to 10%

based on the microcapsules. Polyethylene oxide also may be applied as a subbing layer between the opaque substrate and the microcapsule layer or it may be used in combination as a subbing layer and as a binder in the microcapsule layer. The subbing layer may be applied in a coat weight of about 1 to 4 g/cm² (dry weight).

Other binder materials which may be utilized to prevent direct sticking of the developer layer and the microcapsule layer include polyvinyl alcohol, polyacrylamide, and acrylic lattices.

In yet another aspect of this embodiment, spacers or anti-blocking agents can be used to improve media stability and thereby extend the shelf life of the imaging system in which microcapsules and developer are coated in separate layers. Since the microcapsule layer and the developer layer remain in close proximity to each other after development, improved media stability is desirable to reduce continued reaction between the image-forming material from the ruptured microcapsules and the developer material which cause the image to darken. Typically, useful spacers are particles having a high crush resistance such as glass microspheres, ceramic particles, and the like. Examples of such materials include 560/10,000 glass microspheres from 3M which have a crush resistance of 10,000 psi, a particle size of about 35 microns and includes about 90% "floaters" (low density particles); and zeeospheres from Zeeosphere Industries, e.g., Zeeosphere Grade 200 having a mean particle size of about 5 microns and Zeeosphere 600 having a mean particle size of about 10 microns. These spacers may be incorporated in the developer layer or in the microcapsule layer. The spacers are typically used in an amount of about 1 to 10% based on the microcapsules.

Antiblocking agents are polymeric materials which are coated on the developer layer to prevent the developer

layer from sticking to the microcapsule layer but which do not deny the color precursor access to the color developer to form an image with good density. Representative examples of useful antiblocking agents include elastomeric materials such as Neoprene emulsion from DuPont; Lytron GA-5705, a polystyrene emulsion from Morton International; and Hycar, a nitrile emulsion from B.F. Goodrich.

Another technique to improve media stability resides in conditioning the developer and microcapsule layers at a relative humidity of about 10 to 40% and preferably, about 20%. Most preferably, the layers are conditioned at about 20% R.H., for about 2 to 12 hours or more at ambient temperatures. Sealing of the assembly at low R.H. levels after conditioning assures that the layers are maintained relatively moisture-free during the normal shelf-life of the assembly and this reduces the tendency for the developer layer and the microcapsule layer to remain in contact after development resulting in image darkening as described above.

Useful photohardenable compositions, photoinitiators, chromogenic materials, carrier oils and encapsulation techniques for the layer of microcapsules 14 are disclosed in U.S. Patent No. 4,399,209 which is herein incorporated by reference. Preferred photohardenable compositions are described in commonly assigned U.S. Patent No. 4,772,541, the necessary contents of which to complete the present specification is incorporated herein by reference. The aforesaid photohardenable compositions are non-silver systems. Also useful in the present invention is a silver-based photohardenable microencapsulated system such as that described in U.S. Patents 4,912,011; 5,091,280 and 5,118,590 and other patents assigned to Fuji Photo Film Co.

In accordance with the preferred embodiments of the invention, a full color imaging system is provided in

which the microcapsules are sensitive to red, green, and blue light respectively. The photohardenable composition in at least one and possibly all three sets of microcapsules is sensitized by a cationic dye-borate anion complex as described in U.S. Patent 4,772,541. For optimum color balance, the microcapsules are sensitive (λ max) at about 450 nm, 540 nm, and 650 nm, respectively. Such a system is useful with visible light sources in direct transmission or reflection imaging. Such a material is useful in making contact prints or projected prints of color photographic slides. They are also useful in electronic imaging using lasers or pencil light sources of appropriate wavelengths.

Because the cationic dye-borate anion complexes absorb at wavelengths greater than 400 nm, they are colored. The unexposed dye complex present in the microcapsules in the non-image areas can cause undesired coloration in the background area of the final picture. Typically, the mixture of microcapsules is green which gives the background areas a greenish tint. Means for preventing or reducing undesired coloration in the background as well as the developed image include reducing the amount of photoinitiator used and adjusting the relative amounts of cyan, magenta and yellow microcapsules as shown in the examples which follow.

The photohardenable compositions of the present invention can be encapsulated in various wall formers using techniques known in the area of carbonless paper including coacervation, interfacial polymerization, polymerization of one or more monomers in an oil, as well as various melting, dispersing, and cooling methods. To achieve maximum sensitivities, it is important that an encapsulation technique be used which provides high quality capsules which are responsive to changes in the internal phase viscosity in terms of their ability to rupture. Because

the borate tends to be acid sensitive, encapsulation procedures conducted at higher pH (e.g., greater than about 6) are preferred.

Melamine-formaldehyde capsules are particularly useful. It is desirable in the present invention to provide a pre-wall in the preparation of the microcapsules. See U.S. Patent 4,962,010 for a particularly preferred encapsulation using pectin and sulfonated polystyrene as system modifiers. The formation of pre-walls is known, however, the use of larger amounts of the polyisocyanate precursor is desired. A capsule size should be selected which minimizes light attenuation. The mean diameter of the capsules used in this invention typically ranges from approximately 1 to 25 microns. As a general rule, image resolution improves as the capsule size decreases. Technically, however, the capsules can range in size from one or more microns up to the point where they become visible to the human eye.

The developer materials and coating compositions containing the same conventionally employed in carbonless paper technology are useful in the present invention. Illustrative examples are clay minerals such as acid clay, active clay, attapulgite, etc.; organic acids such as tannic acid, gallic acid, propyl gallate, etc.; acid polymers such as phenol-formaldehyde resins, phenol acetylene condensation resins, condensates between an organic carboxylic acid having at least one hydroxy group and formaldehyde, etc.; metal salts of aromatic carboxylic acids or derivatives thereof such as zinc salicylate, tin salicylate, zinc 2-hydroxy naphthoate, zinc 3,5 di-tert butyl salicylate, zinc 3,5-di-(a-methylbenzyl)salicylate., oil soluble metals salts or phenol-formaldehyde novolak resins (e.g., see U.S. Patent Nos. 3,672,935; 3,732,120 and 3,737,41) such as zinc modified oil soluble phenol-formaldehyde resin as disclosed in U.S. Patent No.

3,732,120, zinc carbonate etc. and mixtures thereof. The preferred developer material is one which will permit room temperature development such as zinc salicylate and particularly a mixture of zinc salicylate with a phenol formaldehyde resin. Especially preferred for use in the embodiments of FIGS. 3-7 is a mixture of zinc salicylate or a zinc salicylate derivative and phenol-formaldehyde resin and, more particularly, a mixture of 25% HRJ 11177, a phenolic resin from Schenectady Chemical Company and 75% zinc salicylate. The particle size of the developer material is important to obtain a high quality image. The developer particles should be in the range of about 0.2 to 3 microns and, preferably in the range of about 0.5 to 1.5 microns. A suitable binder such as polyvinyl alcohol (PVA) is mixed with the developer, typically in an amount of about 1 to 8% by weight, to prepare a coating composition.

In the embodiment of FIGS. 3-7, where the developer is adjacent to the transparent support, when the image is viewed through the transparent support against a background provided by the opaque support, it is apparent that the thickness of the developer layer should be controlled to provide a sufficiently clear view of the image. Accordingly, the amount of developer material coated on the transparent support should be in the range of about 4 to 12 g/m² and is preferably about 8 g/m². If the layer is too thick, the color former may not fully migrate to the support to provide a dense enough image. Likewise, if there is not enough developer material in the layer, the image density will not be sufficient. For these reasons, the aforementioned ranges are recommended.

Microcapsules useful in practicing the present invention are preferably prepared and blended to form a photohardenable layer as illustrated in Example 1 below. In accordance with the invention, the amount of photoinitiator in the microcapsules has been reduced and

the ratio of cyan to magenta and yellow capsules has been adjusted to provide a layer with minimal tint so as not to distract from the whiteness of the background.

EXAMPLE 1

Model Laboratory Capsule Preparation

1. Into a 600 ml stainless steel beaker, 110 g water and 4.6 g isobutylene maleic anhydride copolymer (dry) are weighed.
2. The beaker is clamped in place on a hot plate under an overhead mixer. A six-bladed, 45° pitch, turbine impeller is used on the mixer.
3. After thoroughly mixing, 4.0 g pectin (polygalacturonic acid methyl ester) is slowly sifted into the beaker. This mixture is stirred for 2 hours at room temperature (800-1200 rpm).
4. The pH is adjusted to 7.0 with 20% sulfuric acid.
5. The mixer is turned up to 3000 rpm and the internal phase is added over a period of 10-15 seconds. Emulsification is continued for 10 minutes. Magenta and yellow precursor phases are emulsified at 25°-30° C Cyan phase is emulsified at 45°-50° C (oil), 25°-30° C (water).
6. At the start of emulsification, the hot plate is turned up so heating continues during emulsification.
7. After 10 minutes, the pH is adjusted to 8.25 with 20% sodium carbonate, the mixing speed is reduced to 2000 rpm, and a solution of melamine-formaldehyde prepolymer is slowly added which is prepared by dispersing 3.9 g melamine in 44 g water, adding 6.5 g formaldehyde solution (37%) and heating at 60°C until the solution clears plus 30 minutes.

8. The pH is adjusted to 6.0, the beaker is covered with foil and placed in a water bath to bring the temperature of the preparation to 65° C. When 65°C is reached, the hot plate is adjusted to maintain this temperature for a two hour cure time during which the capsule walls are formed.

9. After curing, mixing speed is reduced to 600 rpm, formaldehyde scavenger solution (7.7 g urea and 7.0 g water) is added and the solution was cured another 40 minutes.

10. The pH is adjusted to 9.5 using a 20% NaOH solution and stirred overnight at room temperature.

Three batches of microcapsules were prepared as above for use in a full color imaging sheet using the three internal phase compositions set forth below.

Yellow Capsule Internal Phase (420 nm)

TMPTA	35 g
DPHPA	15 g
3-thionyl-7-diethylaminocoumarin	15 g
2-Mercaptobenzoxazole (MBO)	2.0 g
2,6-Diisopropylaniline	1.0 g
Reakt Yellow (BASF)	5.0 g
Desmodur N-100 (Bayer Biuret Polyisocyanate Resin)	3.33 g

Magenta Capsule Internal Phase (550 nm)

TMPTA	50 g
1,1'-dibutylindocarbocyanine-methyltriphenylborate complex	0.2 g
2,6-Diisopropylaniline	2.0 g

HD5100 (Magenta color precursor from Hilton-Davis Chemical Co.)	12.0 g
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Cyan Capsule Internal Phase (650 nm)

TMPTA	50 g
1-1'-diheptylindocarbocyanine-hexyltriphenylborate complex	0.31 g
2,6-Diisopropylaniline	2.0 g
Cyan Precursor (CP-177 of Hilton-Davis Chemical Co.)	6 g

Microcapsules prepared as above were used to prepare the following coating composition:

Cyan Capsules	36 g
Magenta Capsules	30 g
Yellow Capsules	34 g
Dow Binder (Dow Additive Q1-6106 from Dow Chemical Co.)	10 g

This composition was coated on an opaque PET support (Melinex) at a coat weight of 10 g/sq m.

The following developer composition was applied to a transparent PET film in a coat weight of 12 g/sq. m:

Phenolic Resin (HRJ 4542 from Schenectady Chemical Co.)	96 g
Polyvinyl alcohol (airvol grade 205 from Air Products Co.)	4 g

The two films were joined together so that the microcapsule coating and the developer coating were in a facing relationship and the edges of the two supports were sealed using Ashland's PS 508 adhesive.

EXAMPLE 2

The following coating composition was prepared and coated on a PET support:

Cyan Capsules	36 g
Magenta Capsules	30 g
Yellow Capsules	34 g
Dow Binder	10 g
HRJ 4542 (Schenectady)	90 g
PVA (airvol grade 205 from Air Products Co.)	10 g

A second PET support was placed over the coated composition and the two layers sealed at their edges using Ashland's PS 508 adhesive.

The imaging system of the present invention can be exposed in any suitable camera or other exposure device to provide an image. The imaging system of this invention is especially suitable for exposure using a liquid crystal array or light emitting diodes driven by a video signal for the reproduction of images from a video cassette recorder, a camcorder, or the like.

Having described the invention in detail and by reference to preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

What is claimed is:

1. A self-contained photohardenable imaging assembly comprising a first transparent support, a second support which may be transparent or opaque and an imaging layer comprising a developer material and a plurality of photohardenable microcapsules, said microcapsules containing a color former and a photohardenable composition, wherein said imaging layer is disposed between said first transparent support and said second support.
2. The assembly of claim 1 wherein said first transparent support is a clear polyethylene terephthalate film and said second support is an opaque polyethylene terephthalate film containing a white pigment.
3. The assembly of claim 2 wherein said pigment is titanium dioxide.
4. The assembly of claim 1 wherein said second support is a transparent film comprising a clear polyethylene terephthalate film.
5. The assembly of claim 1 wherein said developer material comprises a mixture of zinc salicylate or a derivative thereof and a phenolic resin.
6. The assembly of claim 5 wherein said mixture comprises about 75% zinc salicylate or a derivative thereof and about 25% phenol-formaldehyde resin.
7. The assembly of claim 1 further comprising a layer of an adhesive material.
8. The assembly of claim 7 wherein said imaging layer is disposed on one surface of either said first or said second

support and said adhesive is disposed on one surface of the other of said first or second support.

9. The assembly of claim 1 wherein said developer material, said plurality of photohardenable microcapsules, and said adhesive material are mixed and disposed as a single layer on said first support or said second support.

10. The assembly of claim 2 wherein said assembly is useful for forming images in an imaging process which comprises:

image-wise exposing said microcapsules through said first transparent support to actinic radiation;

subjecting said assembly to a uniform pressure to rupture said microcapsules such that said color former is image-wise released from said microcapsules and migrates to said developer to form an image;

viewing the image through said first transparent support, said opaque support providing a white reflective background therefor.

11. The assembly of claim 4 wherever said assembly is useful for forming imaging in an imaging process which comprises:

image-wise exposing said microcapsules through said first transparent support to actinic radiation;

subjecting said assembly to a uniform pressure to rupture said microcapsules such that said color former is image-wise released from said microcapsules and migrates to said developer to form an image;

viewing the image as a transparency.

12. A self-contained photohardenable imaging assembly comprising a first transparent support; a layer of developer material applied to one surface of said first

transparent support; a second support which may be transparent or opaque; and a layer of microcapsules applied to one surface of said second support, wherein said first transparent support is assembled with said second support such that said developer material is disposed in a facing relation with said microcapsules, and said first transparent support is sealed to said second support along a predetermined border at the periphery of said assembly.

13. The assembly of claim 12 wherein said microcapsule layer further comprises a binder.

14. The assembly of claim 13 wherein said binder is selected from the group consisting of polyethylene oxide, polyvinyl alcohol, polyacrylamide, acrylic latices, neoprene emulsions, polystyrene emulsions, and nitrile emulsions.

15. The assembly of claim 12 further comprising a subbing layer between said layer of microcapsules and said opaque support.

16. The assembly of claim 15 wherein said subbing layer comprises polyethylene oxide.

17. The assembly of claim 12 wherein said first transparent support is heat sealed to said second support at the peripheral edges of said assembly.

18. The assembly of claim 12 wherein said first transparent support is a clear polyethylene terephthalate film and said second support is an opaque polyethylene terephthalate film containing a white pigment.

19. The assembly of claim 12 wherein said white pigment is titanium dioxide.

20. The assembly of claim 12 wherein said developer material comprises a mixture of zinc salicylate or a derivative thereof and a phenolic resin.

21. The assembly of claim 20 wherein said mixture comprises about 75% zinc salicylate or a derivative thereof and about 25% phenol-formaldehyde resin.

22. The assembly of claim 12 wherein one of said layer of developer material and said layer of microcapsules includes spacers.

23. The assembly of claim 12 wherein the surface of said layer of developer material facing said layer of microcapsules is coated with an antiblocking agent.

24. The assembly of claim 12 wherein said assembly is prepared by a process wherein said first support having said layer of developer applied thereto, and said second support having said layer of microcapsules applied thereto are held at a relative humidity of about 10 to 40% RH before assembling said first support with said second support and sealing said border such that any tendency for said layer of developer to adhere to said layer of microcapsules is reduced and the stability of the image improved.

25. A method for forming images in a self-contained imaging assembly comprising:

image-wise exposing a self-contained photo-sensitive imaging assembly to a source of actinic radiation, said self-contained photohardenable imaging

assembly comprising a first transparent support, a second support which may be transparent or opaque, and an imaging layer comprising a developer material and a plurality of photohardenable microcapsules containing a color former and a photohardenable composition disposed between said first transparent support and said second support, said second support being bonded to said imaging layer by a layer of adhesive;

subjecting said exposed, self-contained, photohardenable imaging assembly to an uniform rupturing force to cause said photohardenable microcapsules to rupture and image-wise transfer said color former to said developer thereby forming an image; and

viewing said image through said transparent support.

26. The method of claim 22 wherein said second support is a transparent film.

27. The method of claim 22 wherein support is coated on one surface with an imaging composition comprising a developer material and a plurality of microcapsules containing a color former and a photohardenable composition, and support is coated on one surface with an adhesive.

28. The method of claim 22 wherein said second support is an opaque polyethylene terephthalate film containing a white pigment.

29. The method of claim 25 wherein said white pigment is titanium dioxide.

30. The method of claim 22 wherein said developer material, said plurality of photohardenable microcapsules

and said adhesive material are mixed and disposed on a single layer on said first support or said second support.

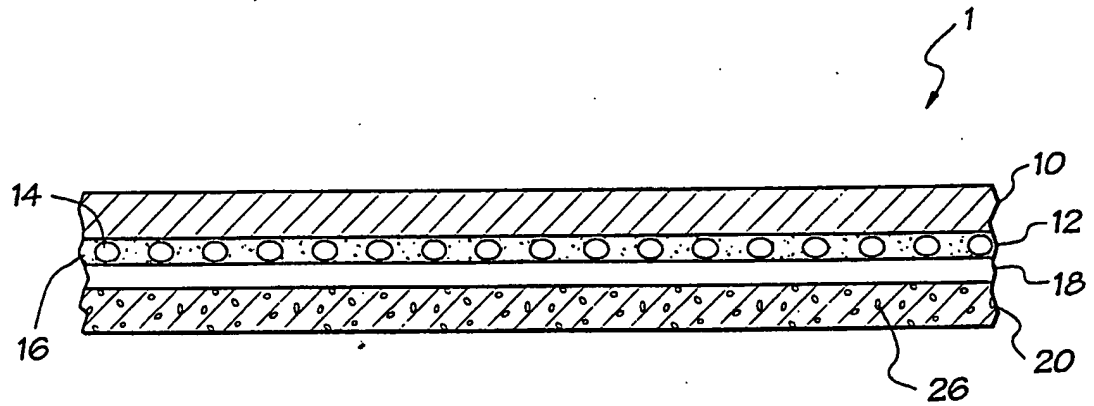


FIG. 1

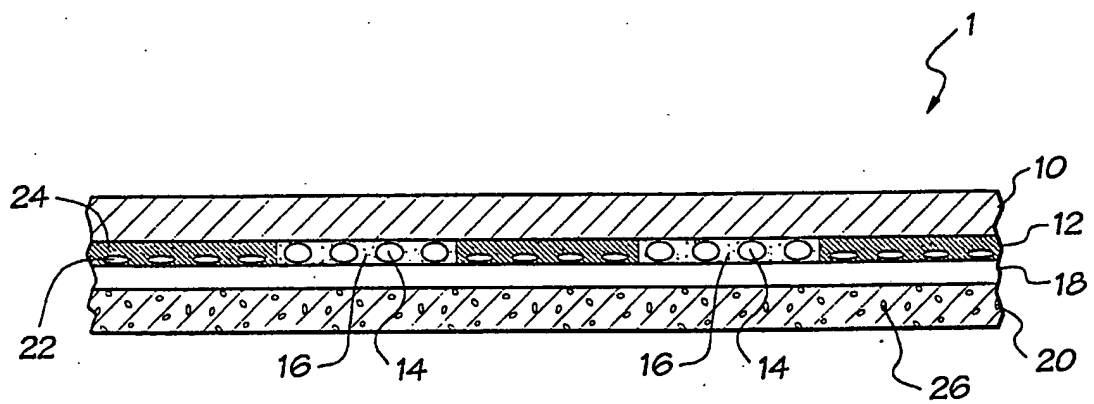


FIG. 2

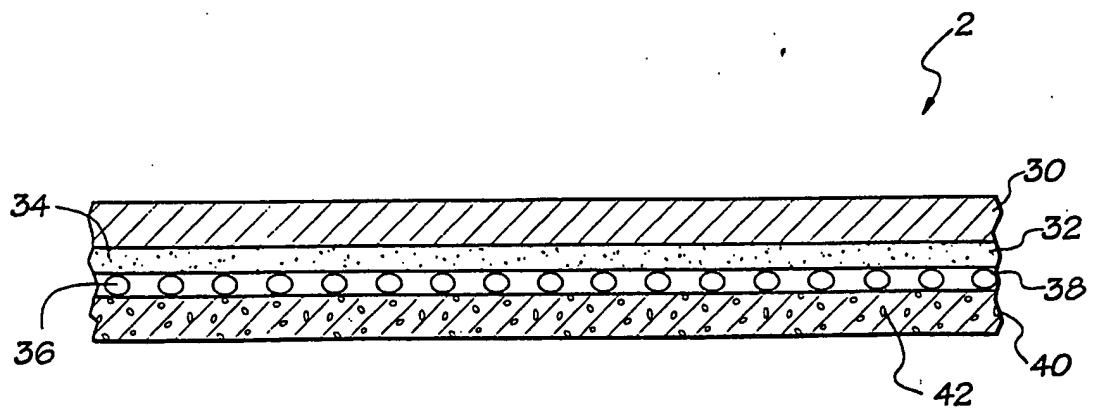


FIG. 3

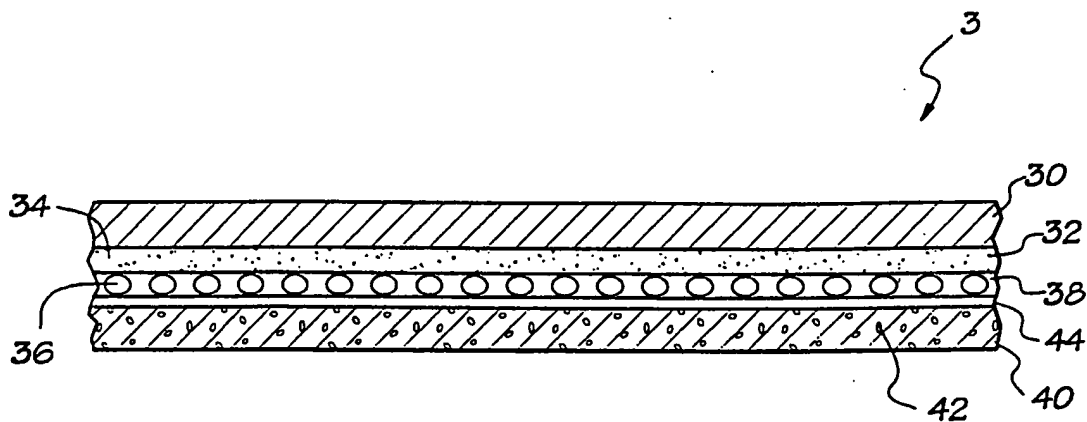


FIG. 4

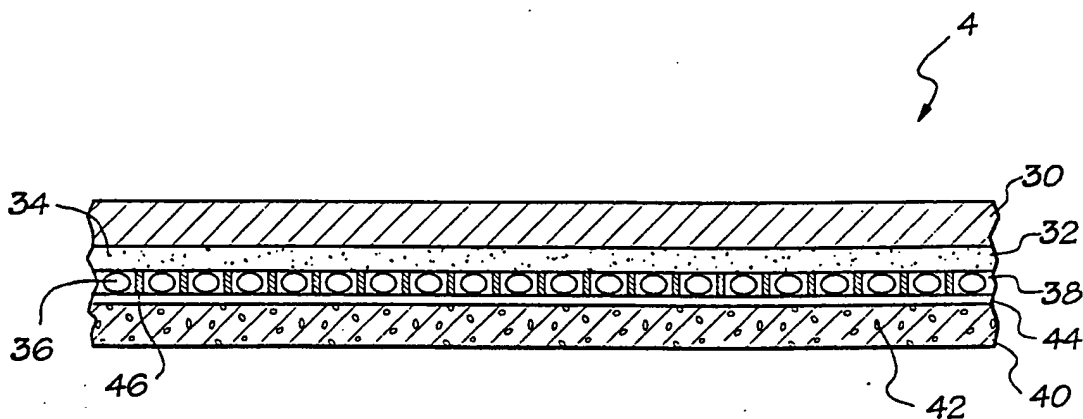


FIG. 5

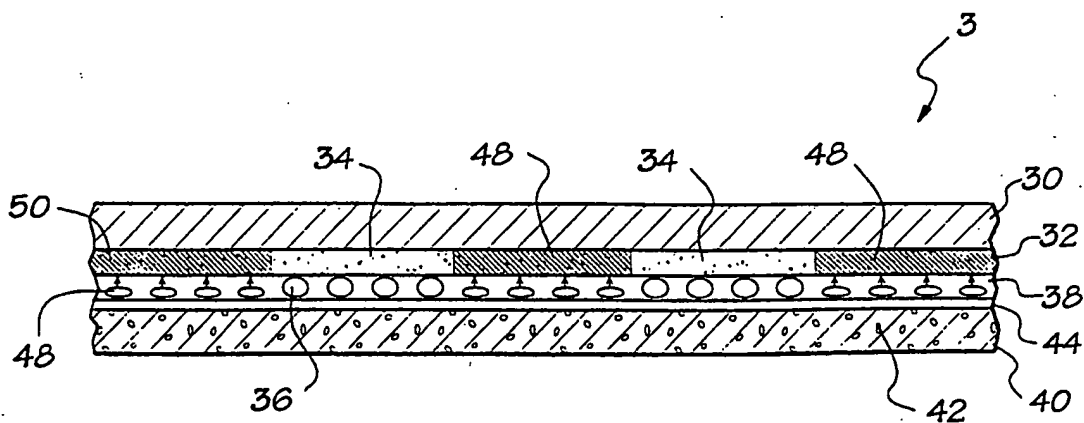


FIG. 6

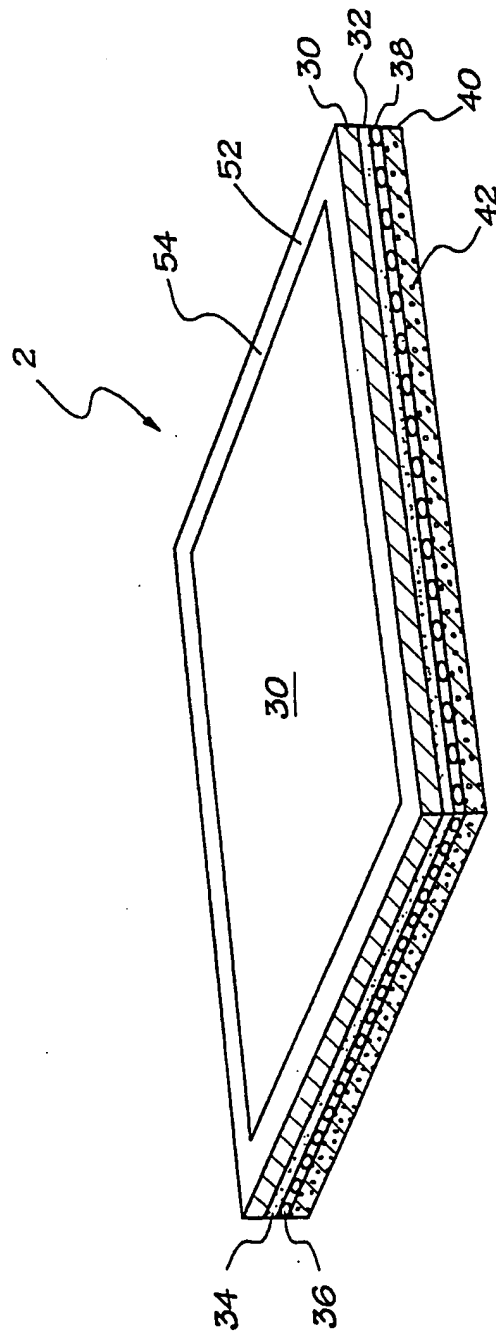


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/02095

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G03F7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 284 446 (THE MEAD CORPORATION) 28 September 1988	1-30
X	cited in the application see the whole document ---	1
Y	US,A,4 920 026 (HIDEAKI HAGIHARA ET AL.) 24 April 1990 see column 4, line 49 - line 14 ---	1-30
Y	RESEARCH DISCLOSURE, vol. 276, HAVANT GB, pages 216-217, E. NELSON 'Two sheet adhered imaging system' see the whole document --- -/--	1-30

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- *&* document member of the same patent family

Date of the actual completion of the international search

20 June 1995

Date of mailing of the international search report

30.06.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Rasschaert, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/02095

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 13 no. 271 (P-889) [3619] ,22 June 1989 & JP,A,01 063948 (BROTHER IND LTD) 9 March 1989, see abstract ---	1
X	PATENT ABSTRACTS OF JAPAN vol. 12 no. 483 (P-802) [3330] ,16 December 1988 & JP,A,63 199344 (SEIKO INSTR & ELECTRONICS LTD) 17 August 1988, see abstract ---	1
Y	US,A,4 535 050 (P.C. ADAIR ET AL.) 13 August 1985 see the whole document ---	1-30
X	DE,A,39 23 016 (MITSUBISHI PAPER MILLS, LTD.,) 22 November 1990 see page 4, line 9 - line 14 ---	1
Y	US,A,4 897 334 (YUMIO MATSUMOTO) 30 January 1990 see figures ---	24
Y	US,A,5 212 040 (DAVID J. SANDERS) 18 May 1993 see column 27, line 36. -----	22

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PCT/US 95/02095

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DE-A-3923016	22-11-90	JP-A- 2293849 US-A- 5013629	05-12-90 07-05-91
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US-A-5212040	18-05-93	NONE	